

# AstroChemical Newsletter #25

November 2017

You can access the full abstracts by clicking the paper titles. Submit your abstracts before the 25th of each month for inclusion in the following newsletter.

## Abstracts

### Impact of oxygen chemistry on model interstellar grain surfaces

**A. Rosu-Finsen and M. R. S. McCoustra**

Temperature-programmed desorption (TPD) and reflection-absorption infrared spectroscopy (RAIRS) are used to probe the effect of atomic and molecular oxygen (O and O<sub>2</sub>) beams on amorphous silica (aSiO<sub>2</sub>) and water (H<sub>2</sub>O) surfaces (porous-amorphous solid water; p-ASW, compact amorphous solid water; c-ASW, and crystalline solid water; CSW). Altering the deposition method of O<sub>2</sub> is shown to result in different desorption energies of O<sub>2</sub> due to differences in O<sub>2</sub> film morphology when deposited on the aSiO<sub>2</sub> surface. O<sub>2</sub> enthalpy of formation is dissipated into the aSiO<sub>2</sub> substrate without changes in the silica network. However, on the H<sub>2</sub>O surfaces, O<sub>2</sub> formation enthalpy release is dissipated into the H-bonded matrix leading to morphological changes, possibly compacting p-ASW into c-ASW while CSW appears to undergo amorphisation. The enthalpy release from O<sub>2</sub> formation is, however, not enough to result in reactive desorption of O<sub>2</sub> or H<sub>2</sub>O under the current experimental circumstances. Further to this, O<sub>2</sub> formation on sub-monolayer quantities of H<sub>2</sub>O leads to enhanced de-wetting and a greater degree of H-bond reconnection in H<sub>2</sub>O agglomerates. Lastly, O<sub>3</sub> is observed from the O + O<sub>2</sub> reaction on all surfaces studied.

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### Methyl isocyanate CH<sub>3</sub>NCO: An important missing organic in current astrochemical networks

**Liton Majumdar, Jean-Christophe Loison, Maxime Ruaud, Pierre Gratier, Valentine Wakelam, Audrey Coutens**

Methyl isocyanate (CH<sub>3</sub>NCO) is one of the important complex organic molecules detected on the comet 67P/Churyumov-Gerasimenko by Rosetta's Philae lander. It was also detected in hot cores around high-mass protostars along with a recent detection in the solar-type protostar IRAS 16293-2422. We propose here a gas-grain chemical model to form CH<sub>3</sub>NCO after reviewing various formation pathways with quantum chemical computations. We have used NAUTILUS 3-phase gas-grain chemical model to compare observed abundances in the IRAS 16293-2422. Our chemical model clearly indicates the ice phase origin of CH<sub>3</sub>NCO.

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## The ortho-to-para ratio of H<sub>2</sub>Cl<sup>+</sup>: Quasi-classical trajectory calculations and new simulations in light of new observations

Romane Le Gal, Changjian Xie, Eric Herbst, Dahbia Talbi, Hua Guo and Sebastien Muller

Multi-hydrogenated species with proper symmetry properties can present different spin configurations, and thus exist under different spin symmetry forms, labeled as para and ortho for two-hydrogen molecules. We investigated here the ortho-to-para ratio (OPR) of H<sub>2</sub>Cl<sup>+</sup> in the light of new observations performed in the z=0.89 absorber toward the lensed quasar PKS 1830–211 with the Atacama Large Millimeter/submillimeter Array (ALMA). Two independent lines of sight were observed, to the southwest (SW) and northeast (NE) images of the quasar, with OPR values found to be  $3.15 \pm 0.13$  and  $3.1 \pm 0.5$  in each region, respectively, in agreement with a spin statistical weight of 3:1. An OPR of 3:1 for a molecule containing two identical hydrogen nuclei can refer to either a statistical result or a high-temperature limit depending on the reaction mechanism leading to its formation. It is thus crucial to identify rigorously how OPRs are produced in order to constrain the information that these probes can provide. To understand the production of the H<sub>2</sub>Cl<sup>+</sup> OPR, we undertook a careful theoretical study of the reaction mechanisms involved with the aid of quasi-classical trajectory calculations on a new global potential energy surface fit to a large number of high-level ab initio data. Our study shows that the major formation reaction for H<sub>2</sub>Cl<sup>+</sup> produces this ion via a hydrogen abstraction rather than a scrambling mechanism. Such a mechanism leads to a 3:1 OPR, which is not changed by destruction and possible thermalization reactions for H<sub>2</sub>Cl<sup>+</sup> and is thus likely to be the cause of observed 3:1 OPR ratios, contrary to the normal assumption of scrambling.

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## Spectroscopy of prospective interstellar ions and radicals isolated in para-hydrogen matrices

Masashi Tsuge, Chih-Yu Tseng, Yuan-Pern Lee

para-Hydrogen (p-H<sub>2</sub>) serves as a new host in matrix-isolation experiments for an investigation of species of astrochemical interest. Protonated and mono-hydrogenated species are produced upon electron bombardment during deposition of p-H<sub>2</sub> containing a precursor in a small proportion. The applications of this novel technique to generate protonated polycyclic aromatic hydrocarbons (H<sup>+</sup>PAH), protonated polycyclic nitrogen heterocycles (H<sup>+</sup>PANH), and their neutral counterparts, which are important in the identification of interstellar unidentified infrared emission bands, demonstrate its superiority over other methods. The clean production with little fragmentation, ease of distinction between protonated and neutral species, narrow lines and reliable relative infrared intensities of the lines, and broad coverage of the spectral range associated with this method enable us to assign the isomers unambiguously. The application of this method to the protonation of small molecules is more complicated partly because of the feasible fragmentation and reactions, and partly because of the possible proton sharing between the species of interest and H<sub>2</sub>, but, with isotopic experiments and secondary photolysis, definitive assignments are practicable. Furthermore, the true relative infrared intensities are critical to a comparison of experimental results with data

from theoretical calculations. The spectra of a proton-shared species in solid p-H<sub>2</sub> might provide insight into a search for spectra of proton-bound species in interstellar media. Investigations of hydrogenated species involving the photolysis of Cl<sub>2</sub> or precursors of OH complement those using electron bombardment and provide an improved ratio of signal to noise. With careful grouping of observed lines after secondary photolysis and a comparison with theoretical predictions, various isomers of these species have been determined. This photolytic technique has been applied in an investigation of hydrogenated PAH and PANH, and the hydrogenation reactions of small molecules, which are important in interstellar ice and the evolution of life. The electronic transitions of molecules in solid p-H<sub>2</sub> have been little investigated. The matrix shift of the origins of transitions and the spectral width seem to be much smaller than those of noble-gas matrices; these features might facilitate a direct comparison of matrix spectra with diffuse interstellar bands, but further data are required to assess this possibility. The advantages and disadvantages of applying these techniques of p-H<sub>2</sub> matrix isolation to astrochemical research and their future perspectives are discussed.

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## **The efficient photodesorption of nitric oxide (NO) ices. A laboratory astrophysics study**

**R. Dupuy, G. Féraud, M. Bertin, X. Michaut, T. Putaud, P. Jeseck, L. Philippe, C. Romanzin, V. Baglin, R. Cimino, J.-H. Fillion**

The study and quantification of UV photon-induced desorption of frozen molecules furthers our understanding of the chemical evolution of cold interstellar regions. Nitric oxide (NO) is an important intermediate species in both gas-phase and solid-phase chemical networks. In this work, we present quantitative measurements of the photodesorption of a pure NO ice. We used the tunable monochromatic synchrotron light of the DESIRS beamline of the SOLEIL facility near Paris to irradiate NO ices in the 6 - 13.6 eV range and measured desorption by quadrupole mass spectrometry. We find that NO photodesorption is very efficient, its yield being around 1e-2 molecule per incident photon for UV fields relevant to the diffuse and dense interstellar medium. We discuss the extrapolation of our results to an astrophysical context and we compare photodesorption of NO to previously studied molecules.

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## **Circumstellar ammonia in oxygen-rich evolved stars**

**K. T. Wong, K. M. Menten, T. Kamiński, F. Wyrowski, J. K. Lacy, T. K. Greathouse**

The circumstellar ammonia (NH<sub>3</sub>) chemistry in evolved stars is poorly understood. Previous observations and modelling showed that NH<sub>3</sub> abundance in oxygen-rich stars is several orders of magnitude above that predicted by equilibrium chemistry. In this article, we characterise the spatial distribution and excitation of NH<sub>3</sub> in the O-rich circumstellar envelopes (CSEs) of four diverse targets: IK Tau, VY CMa, OH 231.8+4.2, and IRC+10420 with multi-wavelength observations. We observed the 1.3-cm inversion line emission with the Very Large Array (VLA) and submillimetre rotational line emission with the Heterodyne Instrument for the Far-Infrared (HIFI) aboard Herschel from all

four targets. For IK Tau and VY CMa, we observed the rovibrational absorption lines in the  $\nu_2$  band near 10.5 micron with the Texas Echelon Cross Echelle Spectrograph (TEXES) at the NASA Infrared Telescope Facility (IRTF). We also attempted to search for the rotational transition within the  $v_2=1$  state near 2 mm with the IRAM 30m Telescope towards IK Tau. Non-LTE radiative transfer modelling, including radiative pumping to the vibrational state, was carried out to derive the radial distribution of NH<sub>3</sub> in these CSEs. Our modelling shows that the NH<sub>3</sub> abundance relative to molecular hydrogen is generally of the order of  $1E-7$ , which is a few times lower than previous estimates that were made without considering radiative pumping and is at least 10 times higher than that in the C-rich CSE of IRC+10216. Incidentally, we also derived a new period of IK Tau from its V-band light curve. NH<sub>3</sub> is again detected in very high abundance in O-rich CSEs. Its emission mainly arises from localised spatial-kinematic structures that are probably denser than the ambient gas. Circumstellar shocks in the accelerated wind may contribute to the production of NH<sub>3</sub>.

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## **Methanol formation in TW Hya and future prospects for detecting larger complex molecules in disks with ALMA**

**Catherine Walsh, Shreyas Vissapragada, & Harry McGee**

Gas-phase methanol was recently detected in a protoplanetary disk for the first time with ALMA. The peak abundance and distribution of methanol observed in TW Hya differed from that predicted by chemical models. Here, the chemistry of methanol gas and ice is calculated using a physical model tailored for TW Hya with the aim to contrast the results with the recent detection in this source. New pathways for the formation of larger complex molecules (e.g., ethylene glycol) are included in an updated chemical model, as well as the fragmentation of methanol ice upon photodesorption. It is found that including fragmentation upon photodesorption improves the agreement between the peak abundance reached in the chemical models with that observed in TW Hya ( $\sim 10$ - $11$  with respect to H<sub>2</sub>); however, the model predicts that the peak in emission resides a factor of 2-3 farther out in the disk than the ALMA images. Reasons for the persistent differences in the gas-phase methanol distribution between models and the observations of TW Hya are discussed. These include the location of the ice reservoir which may coincide with the compact mm-dust disk ( $< 60$  au) and sources of gas-phase methanol which have not yet been considered in models. The possibility of detecting larger molecules with ALMA is also explored. Calculations of the rotational spectra of complex molecules other than methanol using a parametric model constrained by the TW Hya observations suggest that the detection of individual emission lines of complex molecules with ALMA remains challenging. However, the signal-to-noise ratio can be enhanced via stacking of multiple transitions which have similar upper energy levels.

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Full-text URL: <http://cdsads.u-strasbg.fr/abs/2017arXiv171001219W>

## **A general method for the inclusion of radiation chemistry in astrochemical models**

**C. N. Shingledecker, E. Herbst**

In this paper, we propose a general formalism that allows for the estimation of

radiolysis decomposition pathways and rate coefficients suitable for use in astrochemical models, with a focus on solid phase chemistry. Such a theory can help increase the connection between laboratory astrophysics experiments and astrochemical models by providing a means for modelers to incorporate radiation chemistry into chemical networks. The general method proposed here is targeted particularly at the majority of species now included in chemical networks for which little radiochemical data exists; however, the method can also be used as a starting point for considering better studied species. We here apply our theory to the irradiation of H<sub>2</sub>O ice and compare the results with previous experimental data.

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## **Gas mass tracers in protoplanetary disks: CO is still the best**

**T. Molyarova, V. Akimkin, D. Semenov, T. Henning, A. Vasyunin, D. Wiebe**

Protoplanetary disk mass is a key parameter controlling the process of planetary system formation. CO molecular emission is often used as a tracer of gas mass in the disk. In this study we consider the ability of CO to trace the gas mass over a wide range of disk structural parameters and search for chemical species that could possibly be used as alternative mass tracers to CO. Specifically, we apply detailed astrochemical modeling to a large set of models of protoplanetary disks around low-mass stars, to select molecules with abundances correlated with the disk mass and being relatively insensitive to other disk properties. We do not consider sophisticated dust evolution models, restricting ourselves with the standard astrochemical assumption of 0.1  $\mu\text{m}$  dust. We find that CO is indeed the best molecular tracer for total gas mass, despite the fact that it is not the main carbon carrier, provided reasonable assumptions about CO abundance in the disk are used. Typically, chemical reprocessing lowers the abundance of CO by a factor of 3, compared to the case of photo-dissociation and freeze-out as the only ways of CO depletion. On average only 13% C-atoms reside in gas-phase CO, albeit with variations from 2 to 30%. CO<sub>2</sub>, H<sub>2</sub>O and H<sub>2</sub>CO can potentially serve as alternative mass tracers, the latter two being only applicable if disk structural parameters are known.

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## **ALMA discovery of a rotating SO/SO<sub>2</sub> flow in HH212. A possible MHD disk wind ?**

**B. Tabone, S. Cabrit, E. Bianchi, J. Ferreira, G. Pineau des Forêts, C. Codella, A. Gusdorf, F. Gueth, L. Podio, E. Chapillon**

We wish to put tight constraints on the possible contribution of a magnetohydrodynamic disk wind (MHD-DW) to the HH212 molecular jet. We used ALMA Cycle 4 to map the inner outflow at 0.13''  $\sim$  60 au resolution and compared these observations with synthetic predictions for MHD-DW models. We identified, in SO/SO<sub>2</sub>, a rotating flow that is wider and slower than the axial SiO jet. The broad outflow cavity seen in C34S is not carved by a fast wide-angle wind but by this slower agent. Rotation signatures may be fitted by a MHD-DW of a moderate lever arm launched out to  $\sim$  40 au with SiO tracing dust-free streamlines from 0.05-0.3 au. If indeed this is a DW, it could limit the core-to-star efficiency to  $\leq$  50%.

## **A theoretical study of the formation of glycine via hydantoin intermediate in outer space environment**

**M. Kayanuma, K. Kidachi, M. Shoji, Y. Komatsu, A. Sato, Y. Shigeta, Y. Aikawa, M. Umemura**

As a possible formation mechanism of glycine in astrophysical environments, a reaction path via aminoacetonitrile and hydantoin (2,4-imidazolidinedione), which have been detected in an interstellar cloud and meteorites, respectively, were analyzed using the density functional theory. The formation of hydantoin from aminoacetonitrile via the Bücherer-Bergs reaction and the hydrolysis of hydantoin were investigated. The results showed that the catalytic water molecules significantly lower the reaction barriers for the formation of hydantoin. Although the highest barrier is still too high that the pathway is inactive in an interstellar medium, this reaction would proceed during the heating of the meteorite parent body.

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## **Clustering the Orion B giant molecular cloud based on its molecular emission**

**E. Bron, C. Daudon, J. Pety, F. Levrier, M. Gerin, P. Gratier, J. H. Orkisz, V. Guzman, S. Bardeau, J. R. Goicoechea, H. Liszt, K. Öberg, N. Peretto, A. Sievers, P. Tremblin**

Previous attempts at segmenting molecular line maps of molecular clouds have focused on using position-position-velocity data cubes of a single line to separate the spatial components of the cloud. In contrast, wide field spectral imaging with large spectral bandwidth in the (sub)mm domain now allows to combine multiple molecular tracers to understand the different physical and chemical phases that constitute giant molecular clouds. We aim at using multiple tracers (sensitive to different physical processes) to segment a molecular cloud into physically/chemically similar regions (rather than spatially connected components). We use a machine learning clustering method (the Meanshift algorithm) to cluster pixels with similar molecular emission, ignoring spatial information. Simple radiative transfer models are used to interpret the astrophysical information uncovered by the clustering. A clustering analysis based only on the J=1-0 lines of  $^{12}\text{CO}$ ,  $^{13}\text{CO}$  and  $\text{C}^{18}\text{O}$  reveals distinct density/column density regimes ( $n_{\text{H}} \sim 100, 500, \text{ and } >1000 \text{ cm}^{-3}$ ), closely related to the usual definitions of diffuse, translucent and high-column-density regions. Adding two UV-sensitive tracers, the (1-0) lines of  $\text{HCO}^+$  and  $\text{CN}$ , allows us to distinguish two clearly distinct chemical regimes, characteristic of UV-illuminated and UV-shielded gas. The UV-illuminated regime shows overbright  $\text{HCO}^+$  and  $\text{CN}$  emission, which we relate to photochemical enrichment. We also find a tail of high  $\text{CN}/\text{HCO}^+$  intensity ratio in UV-illuminated regions. Finer distinctions in density classes ( $n_{\text{H}} \sim 7\text{E}3, \text{ and } 4\text{E}4 \text{ cm}^{-3}$ ) for the densest regions are also identified, likely related to the higher critical density of the  $\text{CN}$  and  $\text{HCO}^+$  (1-0) lines. The association of simultaneous multi-line, wide-field mapping and powerful machine learning methods such as the Meanshift algorithm reveals how to decode the complex information available in molecular tracers.

## Micrometer-Sized Water Ice Particles for Planetary Science Experiments: Influence of Surface Structure on Collisional Properties

**S. Gärtner, B. Gundlach, T. F. Headen, J. Ratte, J. Oesert, S. N. Gorb, T. G. A. Youngs, D. T. Bowron, J. Blum, and H. J. Fraser**

Models and observations suggest that ice-particle aggregation at and beyond the snowline dominates the earliest stages of planet-formation, which therefore is subject to many laboratory studies. However, the pressure-temperature gradients in protoplanetary disks mean that the ices are constantly processed, undergoing phase changes between different solid phases and the gas phase. Open questions remain as to whether the properties of the icy particles themselves dictate collision outcomes and therefore how effectively collision experiments reproduce conditions in protoplanetary environments. Previous experiments often yielded apparently contradictory results on collision outcomes, only agreeing in a temperature dependence setting in above  $\approx 210$  K. By exploiting the unique capabilities of the NIMROD neutron scattering instrument, we characterized the bulk and surface structure of icy particles used in collision experiments, and studied how these structures alter as a function of temperature at a constant pressure of around 30 mbar. Our icy grains, formed under liquid nitrogen, undergo changes in the crystalline ice-phase, sublimation, sintering and surface pre-melting as they are heated from 103 to 247 K. An increase in the thickness of the diffuse surface layer from  $\approx 10$  to  $\approx 30$  Å ( $\approx 2.5$  to 12 bilayers) proves increased molecular mobility at temperatures above  $\approx 210$  K. As none of the other changes tie-in with the temperature trends in collisional outcomes, we conclude that the surface pre-melting phenomenon plays a key role in collision experiments at these temperatures. Consequently, the pressure-temperature environment, may have a larger influence on collision outcomes than previously thought.

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## Is Photolytic Production a Viable Source of HCN and HNC in Astrophysical Environments? A Laboratory-based Feasibility Study of Methyl Cyanofornate

**Michael J. Wilhelm, Emilio Martínez-Núñez, Jesús González-Vázquez, Saulo A. Vázquez, Jonathan M. Smith, and Hai-Lung Dai**

Motivated by the possibility that cyano-containing hydrocarbons may act as photolytic sources for HCN and HNC in astrophysical environments, we conducted a combined experimental and theoretical investigation of the 193 nm photolysis of the cyano-ester, methyl cyanofornate (MCF). Experimentally, nanosecond time-resolved infrared emission spectroscopy was used to detect the emission from nascent products generated in the photolysis reaction. The time-resolved spectra were analyzed using a recently developed spectral reconstruction analysis, which revealed spectral bands assignable to HCN and HNC. Fitting of the emission band shape and intensity allowed determination of the photolysis quantum yields of HCN, HNC, and  $\text{CN(A)}_2\text{Pi}_1$  and an HNC/HCN ratio of  $\sim 0.076 \pm 0.059$ . Additionally, multiconfiguration self-consistent field

calculations were used to characterize photoexcitation-induced reactions in the ground and four lowest singlet excited states of MCF. At 193 nm excitation, dissociation is predicted to occur predominantly on the repulsive S<sub>2</sub> state, with minor pathways via internal conversion from S<sub>2</sub> to highly excited ground state. An automated transition-state search algorithm was employed to identify the corresponding ground-state dissociation channels, and Rice–Ramsperger–Kassel–Marcus and Kinetic Monte Carlo simulations were used to calculate the associated branching ratios. The proposed mechanisms were validated using the experimentally measured and quasi-classical trajectory-deduced nascent internal energy distributions of HCN and HNC. This work, along with previous studies, illustrates the propensity for cyano-containing hydrocarbons to act as photolytic sources for astrophysical HCN and HNC and may help explain the observed overabundance of HNC in astrophysical environments.

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## Announcements

### **EWASS 2018 Special Session SS5 - Liverpool 3-6 April 2018 - COMs in the Universe: current understanding and perspectives**

EWASS 2018 Special Session SS5 - Liverpool 3-6 April 2018 Complex organic molecules in the Universe: current understanding and perspectives \*\*\* Abstract submission deadline: 27-November-2017 \*\*\* Aims and scope: One of the key questions in modern Astronomy is how life appeared on Earth. It is currently believed that the link between the chemistry observed in the interstellar medium (ISM) and life on Earth may be Complex Organic Molecules (COMs), carbon-based compounds with more than 6 atoms in their molecular structure. Most of the detections of COMs in the ISM have been reported toward either the central region of our Galaxy, the Galactic Center, or toward the hot molecular cocoons around high-mass and low-mass protostars. As a consequence, it has been traditionally assumed that COMs form on the surface of interstellar dust grains predominantly in hot environments. In the past decade, new instrumentation has allowed studies of COMs at much higher sensitivity and spectral resolution, and toward a variety of astronomical objects. The results from these studies have shown that COMs are indeed detected not only in hot galactic environments but also in Solar-system objects such as comets, or even in nearby and high-redshift galaxies. Particularly striking is the detection of these complex organics in harsh environments for COM formation such as UV photon-dominated regions (PDRs), molecular outflows, protoplanetary disks, or cold dark cloud cores. Triggered by these discoveries, the community has made an extraordinary effort to understand the formation of COMs in unfavourable environments. Firstly, large COM surveys have been, or are currently being, carried out at different facilities such as the IRAM 30m telescope, the GBT, NOEMA, and ALMA, to furnish a complete inventory of COMs in star-forming regions at different evolutionary stages and under different physical conditions. Secondly, theoretical studies have proposed new mechanisms for COM formation, including gas-phase formation, non-canonical chemical explosions, cosmic-ray induced radical diffusion, impulsive spot heating of grains, or radical-radical recombination after H-atom addition/abstraction reactions on grain surfaces. Some of these mechanisms are controversial and their actual efficiency is, in most cases, unconstrained. Thirdly, experimental measurements are currently being performed in the lab as a result of these theoretical works, to provide constraints on the efficiency of



these mechanisms, but general consensus does not exist yet. This EWASS Symposium aims at bringing the community together to identify the key limitations in our understanding of COM chemistry and to discuss ideas to overcome those limitations. With the advent of JWST in October 2018, and with ALMA entering its Full Operations phase, this symposium will help us in gaining a complete and detailed view of our current understanding of COM chemistry, and to design the strategy to best exploit these facilities. Programme: COM observations: inventory in galaxies, star-forming regions and Solar-system bodies. COM chemical modelling: Limitations and improvements. Laboratory experiments of COM formation: Limitations and improvements. Invited speakers: Cecilia Ceccarelli (LAOG, France) Kathrin Altwegg (Bern University, Switzerland) Rebeca Aladro (MPIfR, Germany) Catherine Walsh (University of Leeds, UK) Anton Vasyunin (MPE, Germany) David Quenard (QMUL, UK) Harold Linnartz (Leiden Observatory, Netherlands) Louis D'Hendecourt (Université d'Aix-Marseille, France) Nadia Balucani (Università di Perugia, Italy) For abstract submission please visit: <https://kuonicongress.eventsair.com/ewass-2018/abstractsubmission> Scientific organisers: Izaskun Jimenez-Serra (QMUL, UK), Paola Caselli (MPE, Germany), Serena Viti (UCL, UK), Leonardo Testi (ESO, Germany), Jesus Martin-Pintado (CAB, Spain), Marco Minissale (AMU, France) Contact: Izaskun Jimenez-Serra (i.jimenez-serra @ qmul.ac.uk)